Large-Area Dense Plasmonic Nanoarrays for Surface Enhanced Raman Applications

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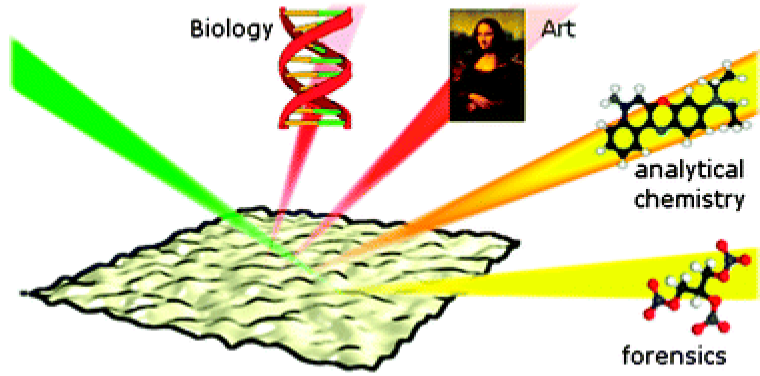
Outline

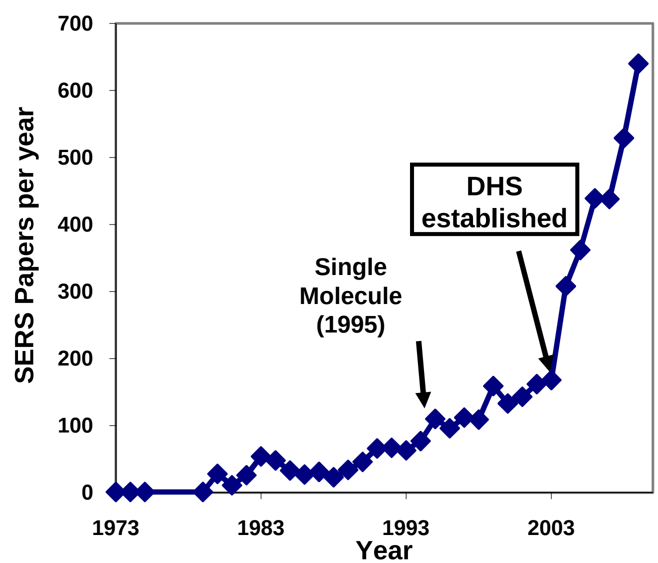
- **Introduction to SERS**
- **Interference lithography as array fabrication platform**
  - **Scheme I : Convective assembly of plasmonic structures**
    Fabrication, Characterization, E-M modeling
  - **Scheme II: Direct metal deposition of plasmonic structures**
    Raman uniformity mapping
- **Summary**

Surface Enhanced Raman Spectroscopy

- **SERS discovered over 30 years ago**
  - Jeanmaire and Van Duyne, 1977
  - Albrecht and Creighton, 1977
- **Orders of magnitude increase in Raman cross-section in the vicinity of plasmonic surfaces**
  - Unenhanced: 10^{-29} cm^2
  - Enhancements of 10^{10} makes it as bright as fluorescence!
- **Tremendous upsurge in SERS science and technology over the last 10 years**
  - Analytical Chemistry
  - Biology
  - Forensics



Quo vadis surface-enhanced Raman scattering?
Phys. Chem. Chem. Phys., 2009, 11, 7348



So, Where are We Now?

- **SERS discovered over 30 years ago**
  - **Orders of magnitude increase in Raman cross-section in the vicinity of plasmonic surfaces**
  - **Dominated by electromagnetic near-field resonant enhancement**
  - **Single molecule sensing at "hot spots" or "hot junctions"**

- **Yet, significant challenges remain before wide implementation**
  - **Practical implementation requires engineering of *high-density "hot-spot substrates"* with *nm* precision over large areas on the order of *cm^2***
    - **Low cost and high throughput**
    - **Reproducibility and signal uniformity**
  - **Formidable nanofabrication challenge due to "*nm-cm* " length scale mismatch**

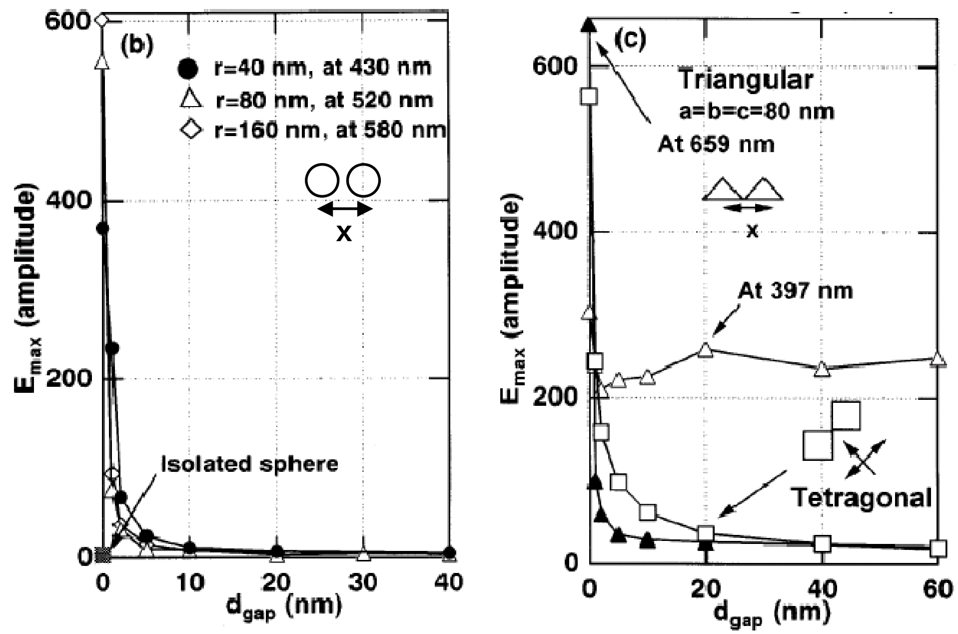
Importance of Hot Spots

- **Rapid increase of E-field enhancement for gap sizes under 10 nm**
- **Since enhancement is localized, "nanogap" density must be maximized for optimum sensitivity**

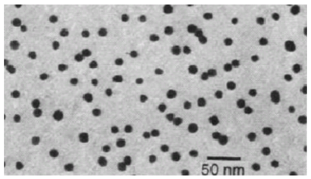
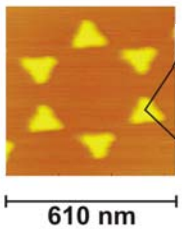
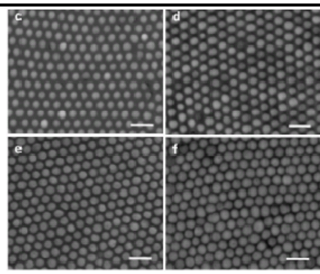
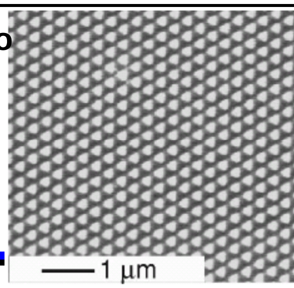
J. Phys. Chem. B 2003, 107, 7607−7617

Local Electric Field and Scattering Cross Section of Ag Nanoparticles under Surface Plasmon Resonance by Finite Difference Time Domain Method

M. Futamata,*,† Y. Maruyama,‡,§ and M. Ishikawa§,∥



Methods of Forming High Densities of Hot Spots

Approach	Authors	Pros	Cons
Self-Assembly 	**Freeman, et al.** **<u>Science</u> (1995)** **267**(5204): 1629-32	**-Cheap and easy**	**-Uniform spacing and gap control are difficult to achieve**
Ag-over nanosphere lithography 	**The Van Duyne group, Northwestern University**	**-Large area coverage** **-Triangular shapes** **-Cheap** **- >10^7 EF reported**	**- Small gap spacing difficult to achieve**
AAO template-assisted 	**Mu et al. (2009) Nanotechnology** **21:** 015604.	**-Large area coverage** **-Gap spacing control** **-Relatively cheap** **-10^7 EF reported**	**-Limited shape control** **-Uniformity issues**
E-beam litho 	**Gunnarsson et al. (2001) <u>Applied Physics Letters</u>** **78**(6): 802-4.	**-Shape control** **-Gap spacing control** **-Very high EF possible**	**-Expensive** **-No scale up potential**

Our Approach to Scalable Substrates

- **Platform: Lithographically defined templates**
  - **157-nm interference lithography**
  - **Crossed exposures allow dense pattering of holes or posts**

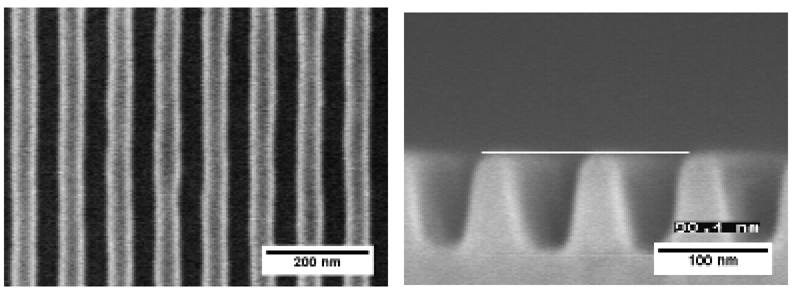
- **Two metal deposition schemes**
  1. **Convective assembly of *individual* nanoparticles into templates**

     Decouple nanoshape fabrication from placement
  2. **Direct evaporation of plasmonic metal through template openings**

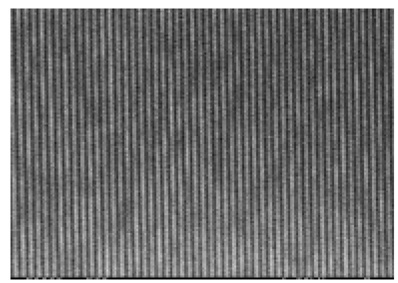
- **Structure design/optimization with electromagnetic simulations**

Interference Lithography for Template Patterning

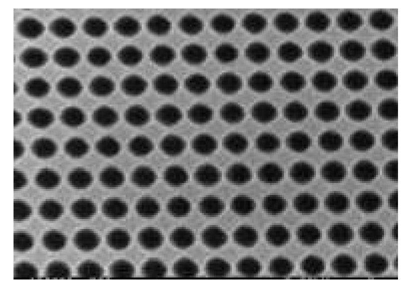
- Unique <u>interference lithography</u> system operating at 157 nm
  - Forms high-resolution periodic arrays with high throughput (compared to e-beam)
  - Half-pitch from 45 to 22 nm → highest optical resolution
- The short wavelength also enables novel photochemistry
  - Direct patterning of PMMA, SiO_2, etc.
  - Chemical surface modification



45-nm lines etched to 90-nm depth



22-nm lines



75-nm circles cut into SiO_2

These capabilities enable new applications
- Lithography
- Nanophotonics
- Nanofluidics
- Biotechnology

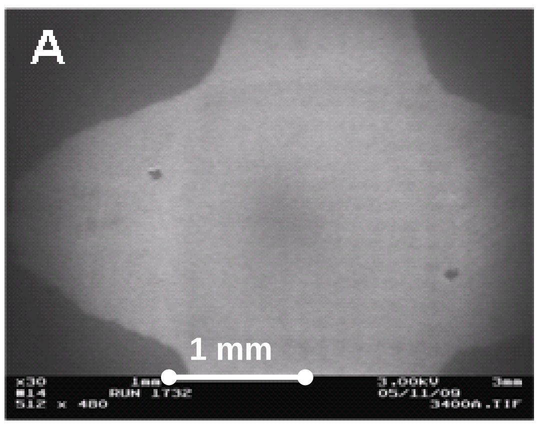
Template Fabrication for Nanoassembly

- Two crossed exposures in PMMA
  - 1.5 mJ/cm^2 dose for each exposure
  - 10 sec for each exposure
  - Exposure followed by 30 sec MIBK/IPA develop

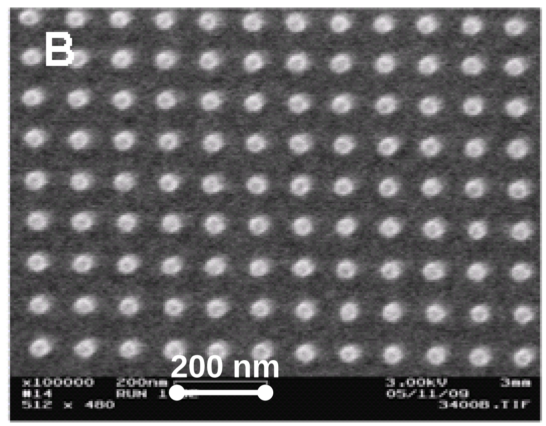
- Only a single litho step – simple processing!

Field Uniformity

Excellent uniformity over 1.5 x 1.5 mm^2



Post Array

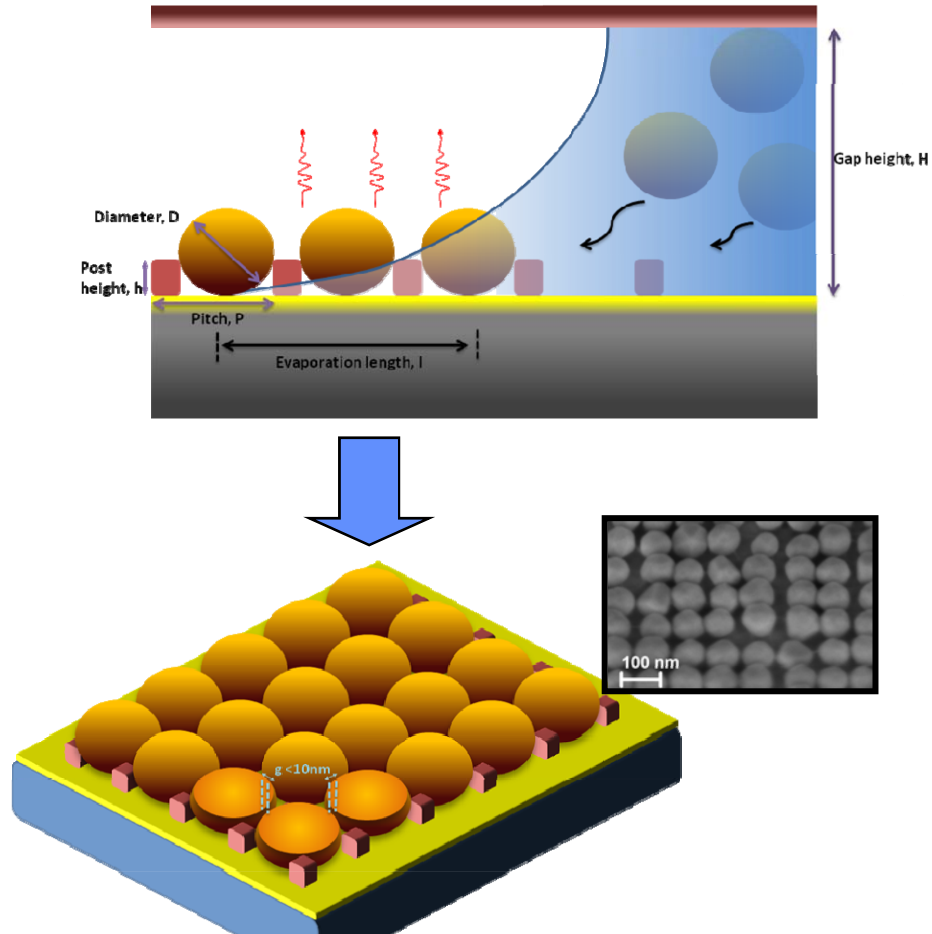


90-nm pitch
35-nm diameter
45-nm height

Convective Assembly from Colloidal Suspension

- **Particle transport towards the surface through convective flow of the colloidal suspension towards the liquid meniscus**

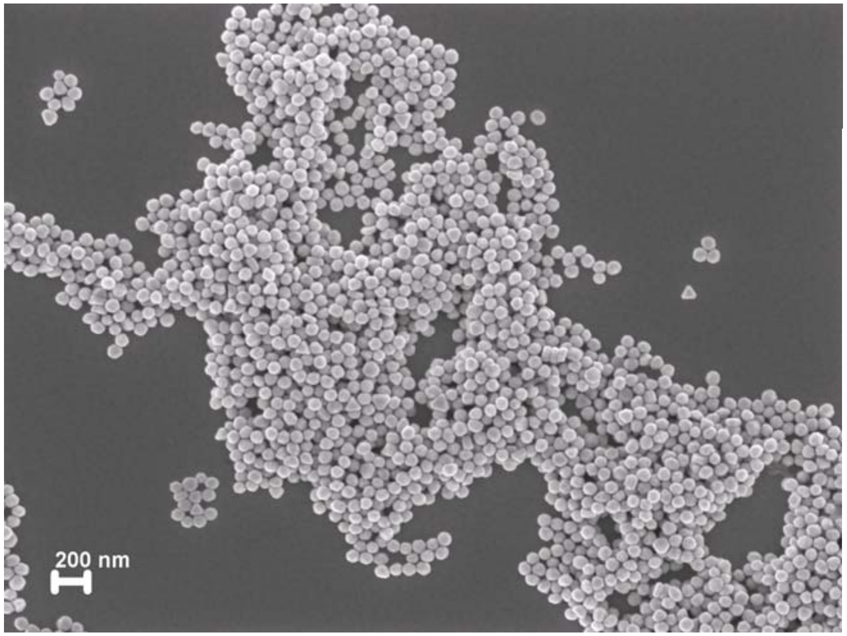
- **Assembly assisted by**
  - **Surface energy difference between hydrophilic gold and hydrophobic PMMA**
  - **Clamping action of the PMMA posts**
  - **Capillary forces of the nano-crevices**



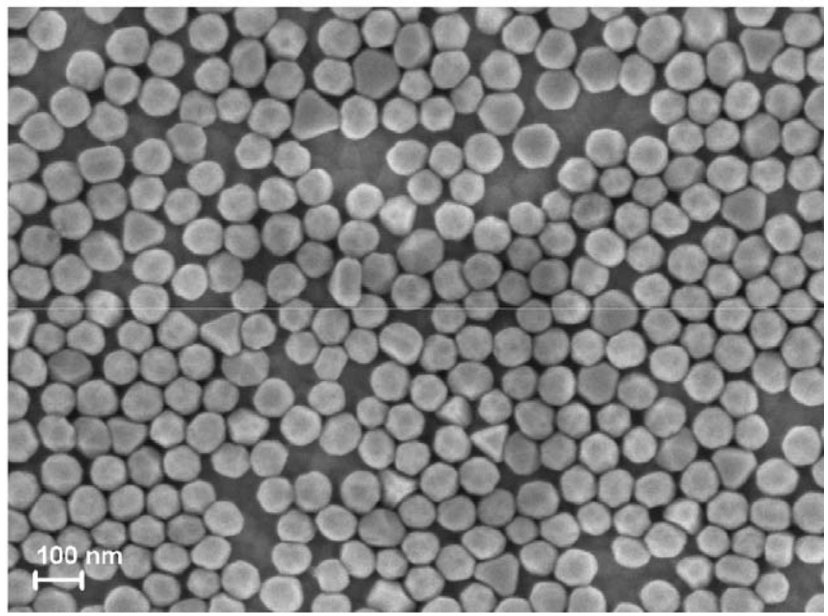
(to appear in *Advanced Materials*, 2010

Assembly Without Nanotemplate

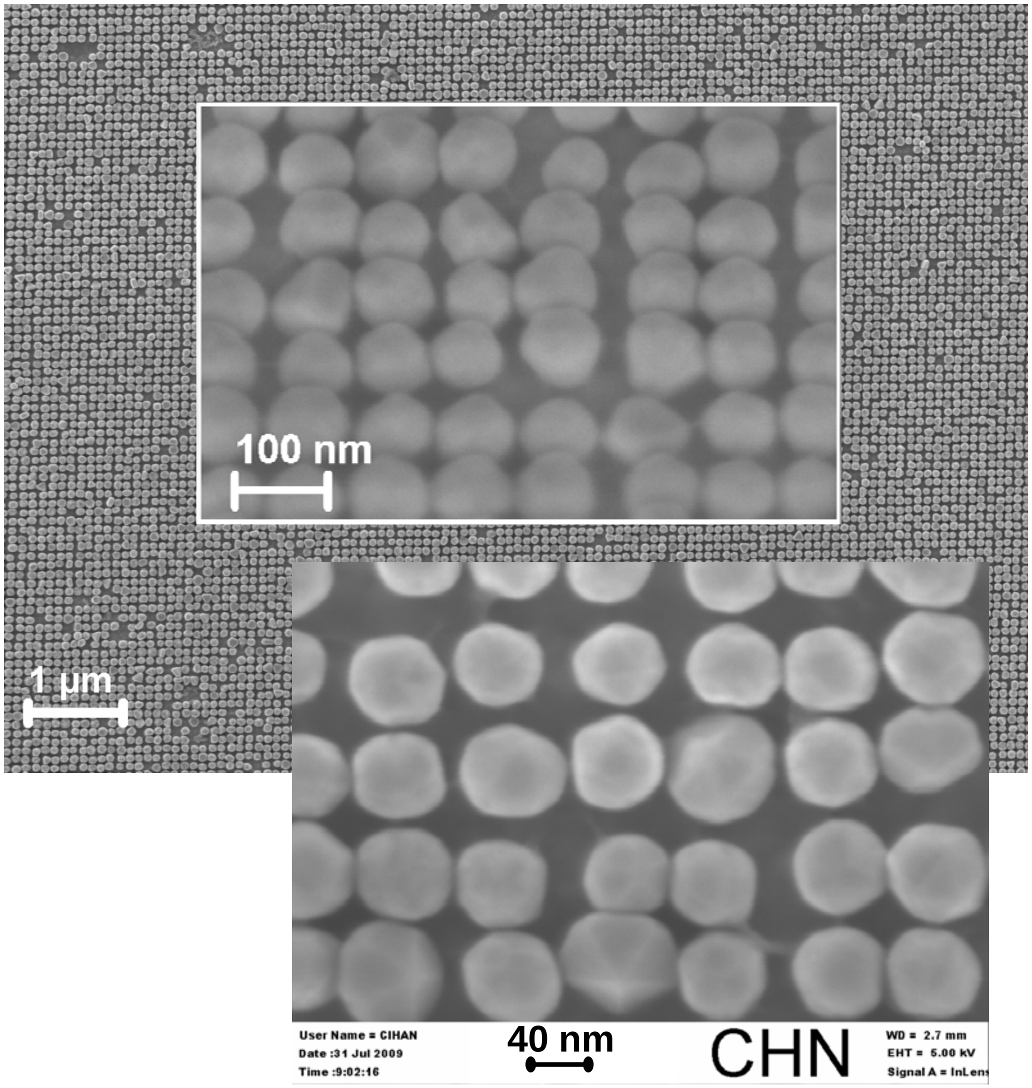
On Hydrophobic PMMA



On Hydrophilic Au Film



Convective Assembly Onto Templated Surface



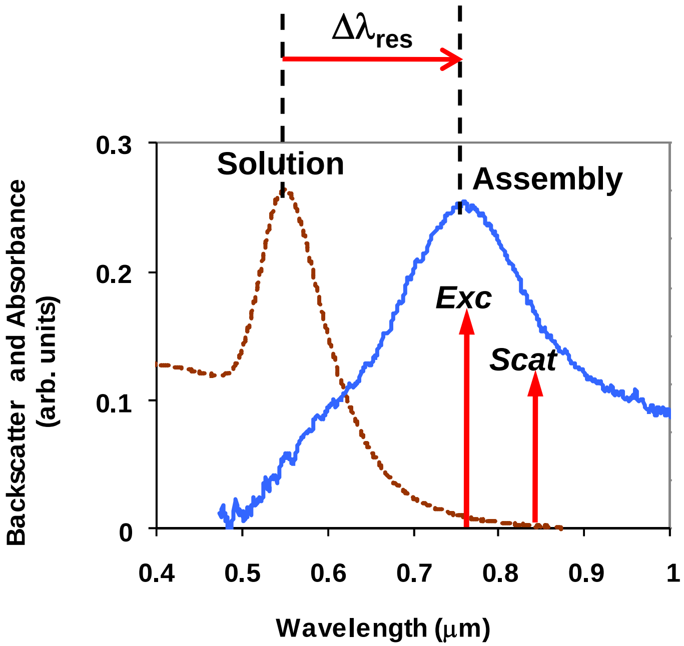
- **Contiguous templating over 15x15 μm^2 areas**
  - **Multiple assembled areas per lithographic field**
- **Gap size variation dominated by particle non-uniformity**
  - **80 nm $\pm$ 8 nm in solution, as quoted by supplier**
  - **Gap size estimated at 10 $\pm$ 5 nm, 1σ**
- **Further reduction in gap size and variation can be achieved**

Measuring Plasmonic Resonances

- **Darkfield Rayleigh backscatter measurements**
  - **Darkfield mode suppresses Au reflection background**
  - **Microreflectance for spatial resolution**

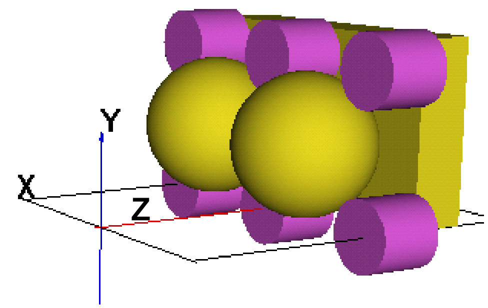
- **Resonance peak strongly red-shifted cf. solution resonance**
  - **From 550 nm for particles in solution to ≈750 nm for nanoassembly**
  - **Nearest-neighbor interactions**

- **Good overlap of resonance with both Raman excitation and Stokes scattered photons**

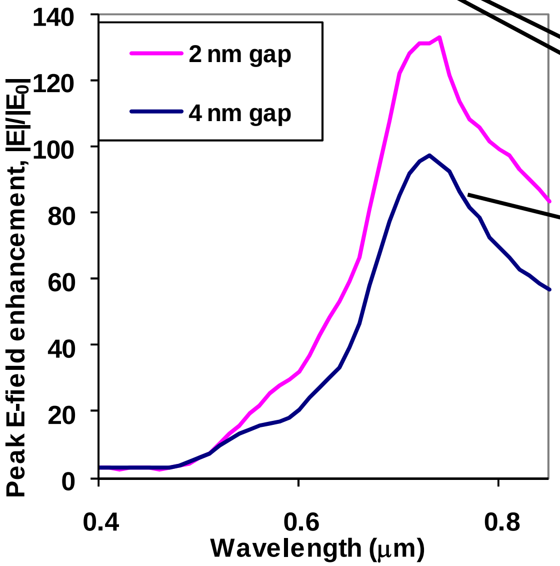


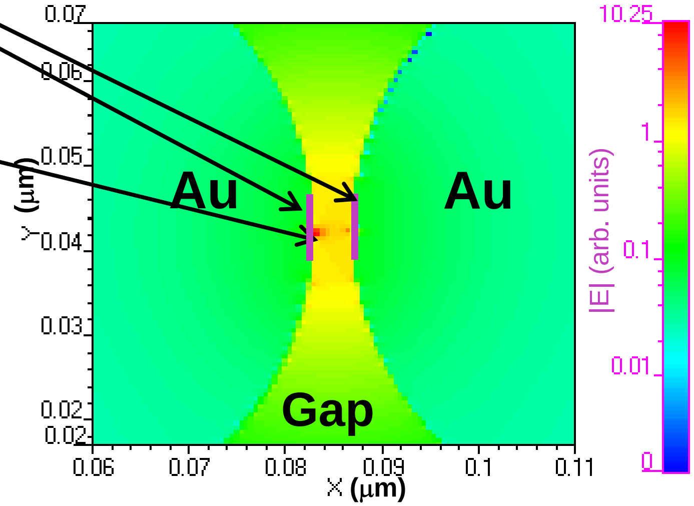
Modeling E-field Enhancement with FDTD

- **Good agreement in wavelength peak position with measured backscatter**
- **Hot spots spatially localized**
  - **2% area contributes to >95% of SERS signal**
  - **7x7 nm^2 area of adsorbates per "hot spot"**

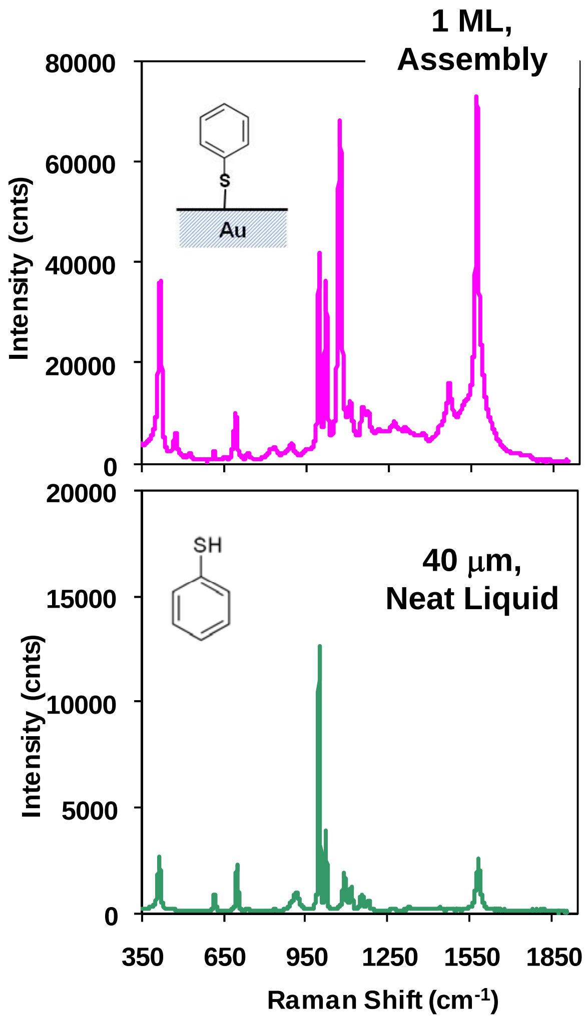


- Au: yellow
- PMMA: purple
- 5 Å grid size

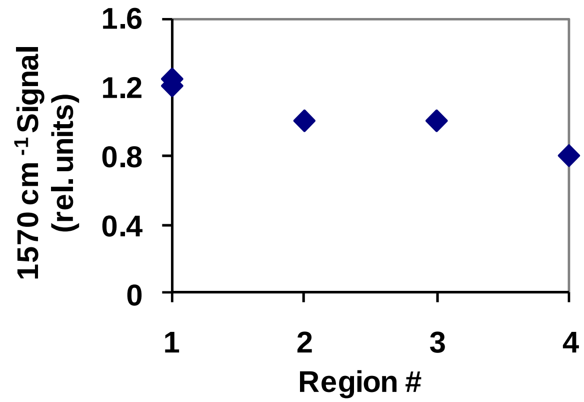




SERS Spectra of Benzenethiol From Nanoassembled Regions



Different Assembly Regions (15x15 μm^2) Within One Field (1.5x1.5 mm^2)



- **Average Enhancement Factor~ 5 x 10^6**
  - **Over 6 µm measurement spot**
  - **Compares well with other published work for nanoarrays**
  - **Using the same conservative definition of EF**

- **± 20% repeatability over different assembly regions**

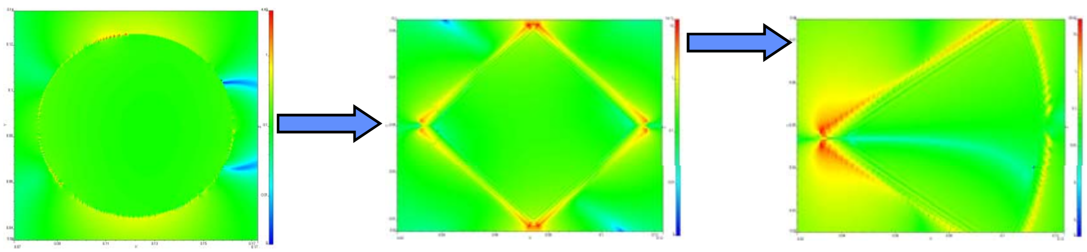
Possible Extension of Nanoassembly – Novel Nanoshapes

- **Surface field enhancement depends strongly on nanoparticle shape**
  - **Sharp corners and tips help to focus fields to form hot spots**

Increasing Surface Field Enhancement from Simulations

$|E_{max}|/|E_{inc}|$

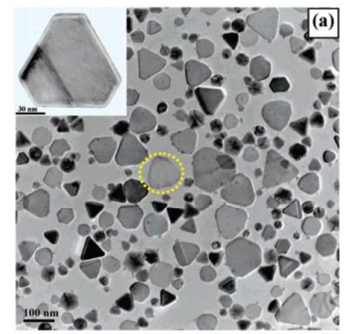
25 **70** **140**

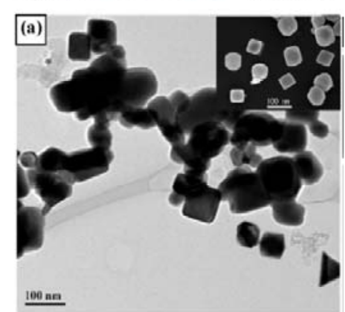


Previous work

Yang, et al.

J. Phys. Chem. C, Vol. 111, No. 26, 2007



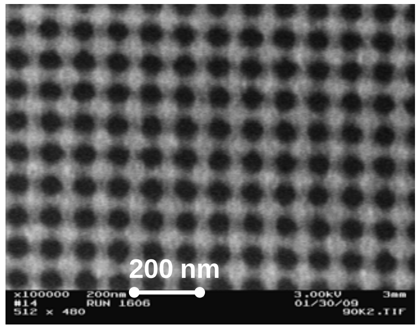


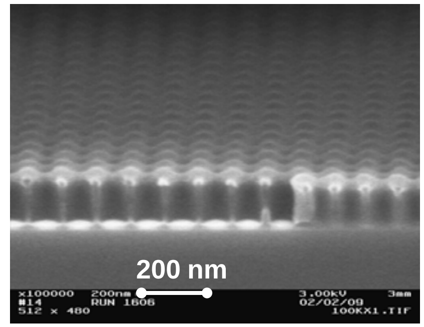
- **Based on previous work, custom synthesis of non-spherical particles in solution is feasible**

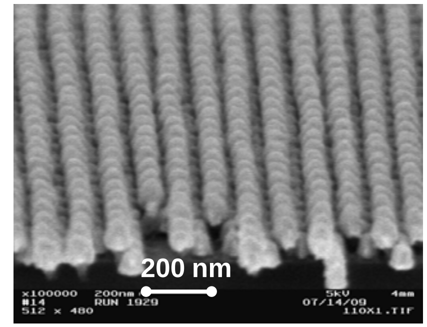
Direct Nanocone Patterning of SERS Structures

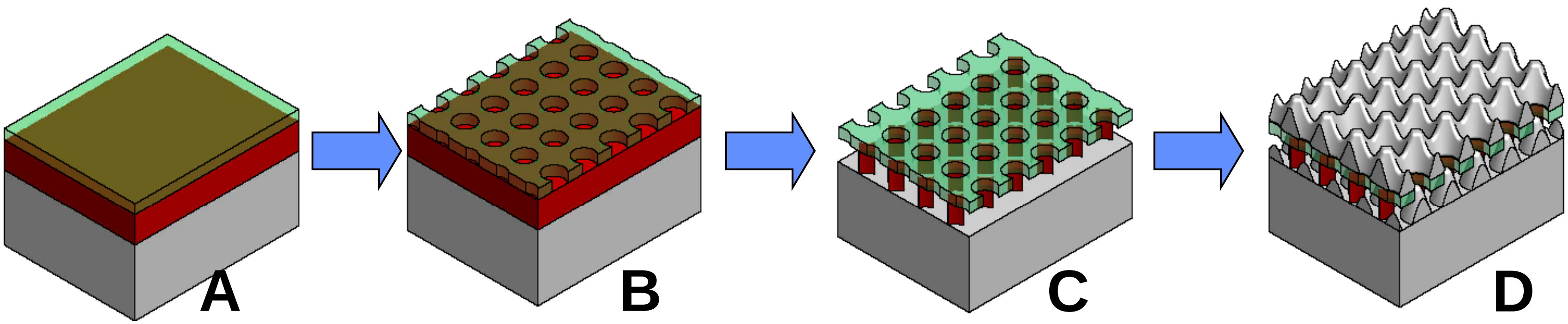
- **As an alternative to templated nanoassembly, we fabricated metal structures using direct metal deposition**
  - **Interference lithography used to pattern openings in a dielectric stack**
- **Offers flexibility of different metal depositions**
  - **Not only *Au* but also *Ag***
- **No lift-off: metal surface is not exposed to chemicals**
- **Potential for formation of 3-dimensional structures**
  - **Cone tips inside cavities**

Nanocone Array Fabrication









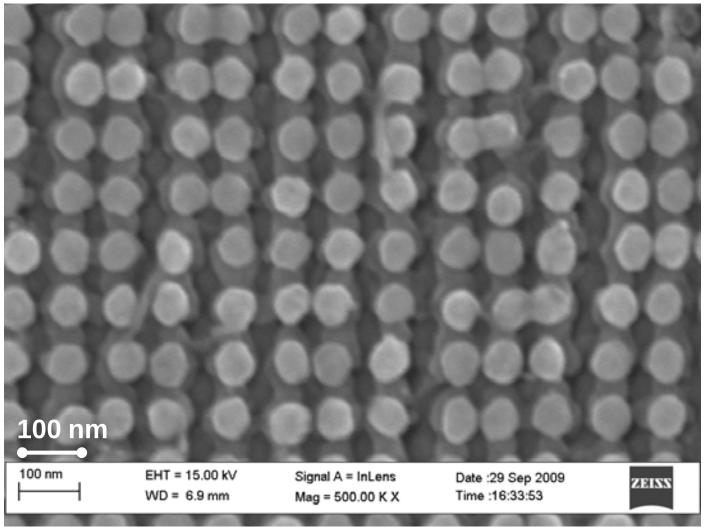
Stack deposition
- 55 nm SOG/80 nm AR3/Si Wafer

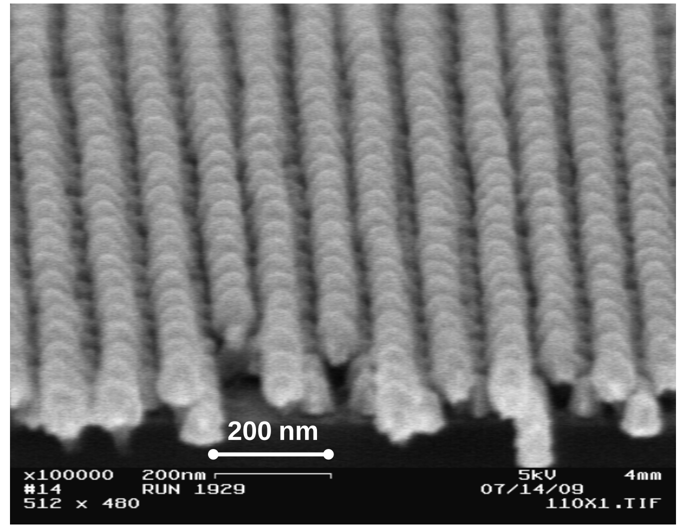
Litho exposure/develop
- Two cross exposures
- TMAH development

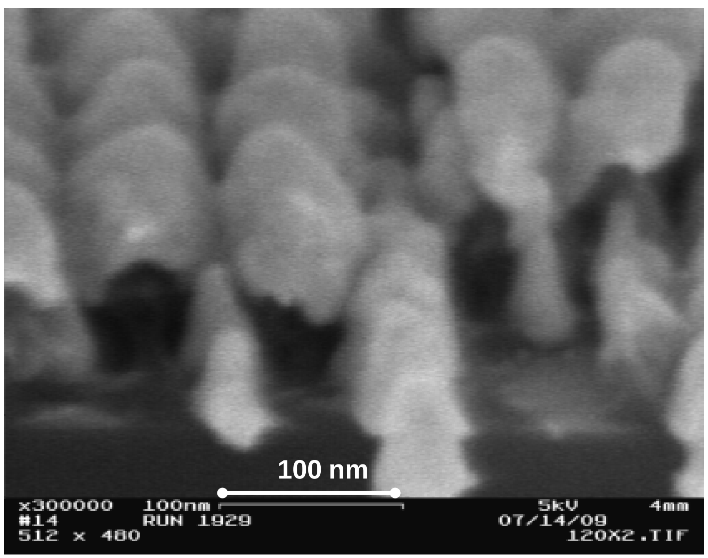
RIE O_2 etch
- Through AR3

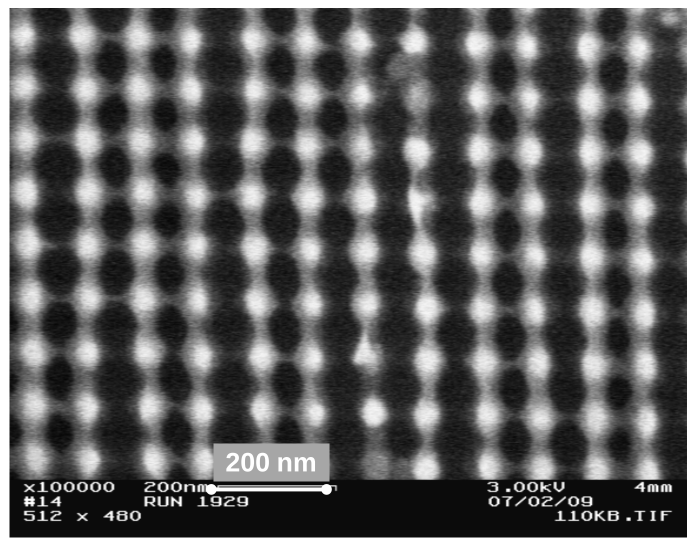
Ag/Au deposition
- E-beam assisted

SEMs of Final 3-D Nanostructures







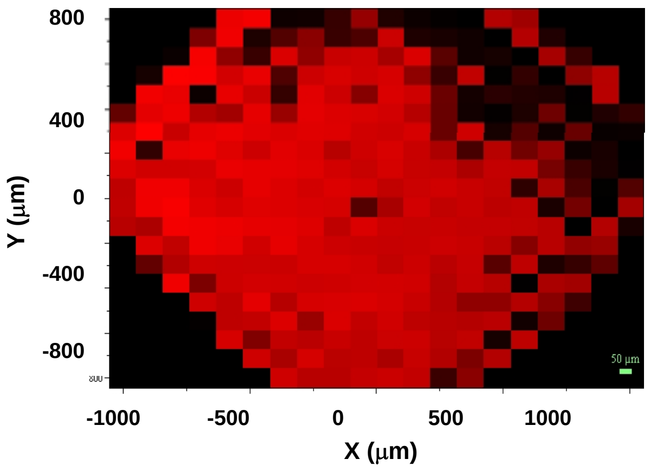


SERS Uniformity Mapping

- **Benzenethiol-treated Ag**
  - **532-nm excitation**
  - **30 μm measurement spot**

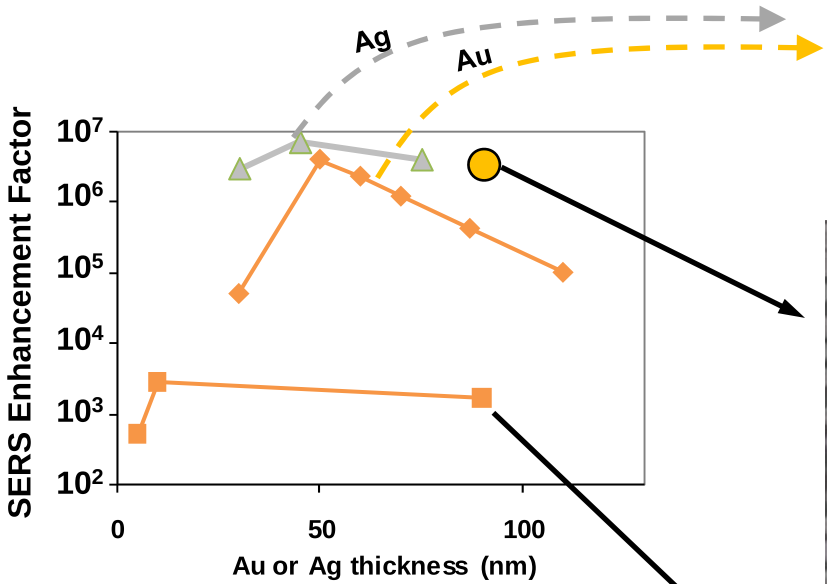
- **Good signal uniformity over the full patterned field**
  - **~1.5 x 1.5 mm^2 area**

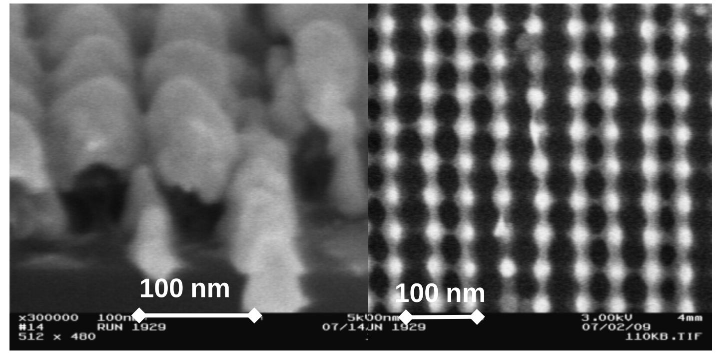
1570 cm^{-1} (ν_{CC}) Intensity Map



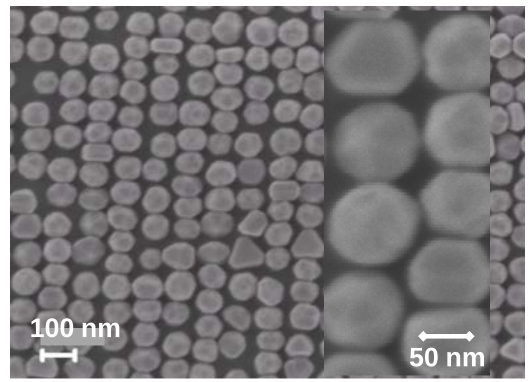
Summary of Average SERS Enhancement Factors

- Analyte: adsorbed benzenethiol
- Wavelength: 785 nm (Au), 532 nm (Ag)

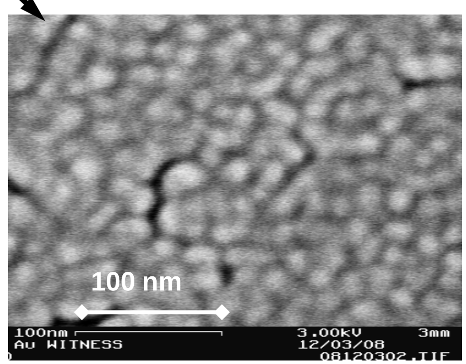




Array of 3-D nanostructures



Array of Au nanospheres



Rough Au film
0.6 nm RMS

Summary

- **Developed two methods of fabricating high-density of SERS "hot spots"**
  - **Nanoassembly-assisted fabrication technique decouples shape/material optimization from placement**
  - **Direct pattern/deposition techniques offers the possibility of tailored 3-D structures for optimum field enhancement**
- **Techniques are scalable to wafer-size area with high throughput**
  - **Multiple mm^2 areas with step-and-repeat**
- **Demonstrated average enhancement factors of > $5x10^6$ over mm^2 areas**
  - **Comparable to state-of-the art over large areas**
  - **Further optimization should improve performance**

Acknowledgments

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